EFFECTS OF RESIDENCE TIME ON THE CHARACTERISTICS OF PAN-BASED FIBERS AND ITS FABRICATION THROUGH SOLVENT-FREE COAGULATION PROCESS

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Abstract

The paper reports the fabrication and characterizations of PAN fibers fabricated using residence time in the range of 2 – 5 s in the solvent-free coagulation process. The PAN fibers were characterized using SEM, FTIR-ATR and tensile testing machine. The SEM photographs revealed that the cross-section of PAN fiber for all sample was free from large void. A residence time of 3 s was found to be the most suitable residence time for fabricating the PAN fibers in the solvent-free coagulation bath. FTIR-ATR data suggested that the PAN fibers possess better molecular orientation and exhibited the highest Young's modulus of 2.55 GPa.

Keywords: PAN fibers, Solvent-free coagulation bath, Residence time

1. Introduction

Acrylic fibers are an important commodity and have been commercially produced for nearly 50 years [1,2]. This type of fiber is highly resistant to sunlight and atmospheric gases, which makes it ideal for awnings and other outdoor uses. Other uses for the filament include evening wear, sports fabrics, rainwear, apparel and carpets. PAN fiber is a form of acrylic fiber and it is widely used as a carbon fiber precursor. The PAN fibers presently take up an overwhelming share which is more than 90 % of the worlds total carbon fiber production [3,4]. The PAN fibers used for carbon fibers production however contain less percent of comonomer in order to acquire the best quality of carbon fibers [5].

PAN is transformed into fibers form by conventional spinning techniques such as melt spinning, wet spinning and dry spinning.

However, nearly all PAN fibers used in commercial produce through wet spinning [6]. Another approach of spinning process to produce excellent properties of the PAN fibers is a dry-wet spinning which had been demonstrated by Bajaj *et al.* [7]. Through this method, the dope is extruded into an air gap and followed by a normal coagulation process.

In general, the coagulation bath contains non-solvent and solvent. The common non-solvent used as precipitation agent is water. Meanwhile, the solvents used for controlling the mass transfer in coagulation bath are sodium thiocyanate, dimethylacetamide (DMAc), ethylene glycol and dimethylformamide (DMF) [6]. The solvent used for controlling the mass transfer in the coagulation bath is similar with those used in the spinning dope [10]. The interaction between the non-solvent and the solvent plays an important role during coagulation process thus influences the morphology and mechanical properties of the PAN fibers. Takahashi *et al.* [11] studied the effect of fiber-forming conditions on the microstructure of acrylic fibers. The cross-section of the fibers revealed the existence of voids if the coagulation bath free from solvent. However, as the concentration of dimetylsulfoxide is increased in the spinning bath, the number of voids was found to decrease. The solvent in the coagulation bath acted as a resistance to the solvent inside the as-spun fibers from diffuses to the coagulation bath and sequentially reduces the possibilities of instantaneous coagulation.

The coagulation bath temperature has also a great effect to the coagulation process. Coagulation bath temperature is responsible for controlling the mass transfer and the counter-diffusion of the solvent and the non-solvent thus influences microscopic and morphological structures as well as the mechanical properties of PAN fibers [7,9]. Numerous studies showed that a reduction in the number of large voids in the cross-section of PAN fibers could be observed as the coagulation bath temperature is decreased [7,9,12]. As the coagulation temperature is reduced, the outward diffusion of solvent predominates resulting in the gel fibers with a small pore size, higher density, less skin formation and low diameter of fibers [7]. This also leads to an improvement in the mechanical properties of PAN fibers because a less quantity of micro-pores inside the fibers [9]. The reduction in coagulation bath temperature also causes the PAN fibers to exhibit a bean-shaped cross-section. However, at higher coagulation bath temperature, the PAN fibers exhibited the maximum number of large voids, an increment in diameter and reduction in the mechanical properties. Meanwhile, the cross-section of PAN fibers become more circular if the spinning process is carried out at higher coagulation bath temperatures [7,9,12,13] and a high solvent content in the coagulation bath [14].

The properties of PAN fibers are also influenced by a jet stretch. The jet stretch (also known as a draw ratio) is the ratio of the first take-up velocity of the wind-up drum to the theoretical polymer dope velocity at the exit of spinneret [7]. The high jet stretch leads to an improvement in the molecular orientation and causes certain functional groups in the PAN fibers to be oriented along the fiber axis [5, 15,16,17]. In contrary to other synthetic fibers, stretching the PAN fibers causes all functional groups except carbon chains lie perpendicular to the chain axis [7]. Therefore, in a drawn fiber the absorption of plane-polarized IR spectrums will be more in the perpendicular direction. The ratio of the parallel absorption to perpendicular absorption will be low in comparison to that of undrawn fibers. The high jet stretch also improves the mechanical properties of PAN fibers, regardless of the coagulation bath temperature [7,18]. The high jet stretch causes the structural reorganization in the direction of the stretch and contributed toward the total strength. A high draw ratio also causes a perfection of structure and in turn influences the tenacity of the fibers [18]. The probability for appearance of defects in the structure increases if a low jet stretch is used during fibers fabrication process [18].

Besides the jet stretch, the formation of PAN fibers is also influenced by the drawing speed [19]. The macro-molecular chain and super-molecular structures orient in the direction of the external force during the drawing process. Simultaneously, at the drawing conditions that favor an instantaneous coagulation, the mobility of structure elements increases and stimulates the disorientation of fiber structure. An increase in the drawing speed leads to an increase in the molecular orientation. When the structure of as-spun fibers is denser and more homogeneous, the drawing speed enhances the molecular orientation to a higher degree.

Recently, the development of solvent-free coagulation process is considered due to the environmental impact of solvent usage. Although the solvent in the coagulation bath is one of the factors that control the coagulation process, the implementation of low residence times during the fibers fabrication process could compensate the absence of solvent in the coagulation bath. This is a new approach to the conventional spinning process which requires a huge coagulation bath so as to complete the coagulation process. In addition, by using the conventional method for producing fibers, extensive amount of coolant must be used for cooling purposes if the coagulation process needs low temperature. In view of further development of the solvent-free coagulation process, this research was conducted to study the effects of residence times on PAN fibers formation and its physical characteristics.

2. Experimental

2.1. Spinning dope preparation

In order to facilitate uniform dissolution of the PAN and AM without formation of gel particles, the polymers was firstly dispersed in cold DMF to create a fine slurry [20] and then, the heat was supplied continuously on the slurry at 80 °C for 5 hours to produce a highly viscous solution. The spinning solution was stored in a solution bottle and then degassed in order to remove bubbles using ultrasonic bath (Branson 3510 Ultrasonic).

2.2. Dry-wet spinning

The dry-wet spinning method was used to fabricate the PAN fibers. The schematic diagram of spinning machine as shown in Fig. 1 consists of a coagulation bath, spinneret, wind-up drum, gear pump, roller and refrigerator. During the fibers fabrication process, the polymer solution was delivered from the storage bottle by gear pump to spinneret under pressure of nitrogen gas. The dope reservoir pressure was kept at 1 atm as a precaution against cavitations in the line to the pump. Then, the gear pump smoothly delivered the spinning solution to the spinneret. Throughout the experiment, the stretching process was maintained at a draw ratio of 4 in order to reduce fibers diameter, to improve molecular orientation as well as for pores removal. The PAN fibers then passed through a series of rollers in the coagulation bath. Then, the PAN fibers were collected onto a wind-up drum which is 17 cm in diameter. Next, the fibers were stretched and tied at a metal net and underwent a drying process. The air-circulated oven was set at 50 °C and the PAN fibers were dried for three hours. The detail specification of spinning process is illustrated in Table 1.

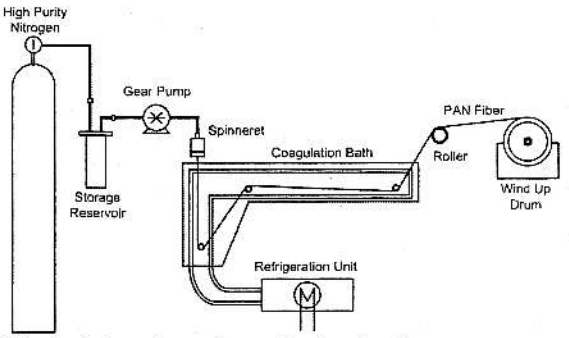

Fig. 1. Laboratory dry-wet spinning line

Table 1
The dry-wet spinning process specification

Spinning Dope	PAN/AM/DMF
AM weight % in Polymer	2.0
Polymer Concentration	18 wt.%
Dope Temperature	Ambient temperature
Spinneret Diameter	200 μm
Air Gap Distance	0.5 – 15 cm
Dope Extrusion Rate	0.012 cm^3/min
Extrusion Velocity, V_s	35 cm/s
Wind-Up Drum Velocity, V_d	140 cm/s
Jet Stretch (V_s/V_d)	4
Retention Time, s	2 – 5 sec
Coagulation Bath Composition	100 % H_2O
Coagulation Bath Temperature	17 °C

2.3. Characterization methods

2.3.1. Scanning electron microscopy

Scanning Electron Microscopy was used to observe the morphology of PAN fiber cross-section. The PAN fiber were immersed in liquid nitrogen for 30 min and then fractured carefully. For each sample type, three samples were prepared. Then the PAN fiber then attached to copper-double-sided-tape in order to support the PAN fiber. The sample was sputtered with gold by using an ion sputtering (Biorad Polaron Division) before viewed on the Scanning

Electron Microscope (Phillips SEMEDAX; XL 40; PW6822/10) with potential of 10 kV under magnifications ranging from 500x to 1500x.

2.3.2. Attenuated total reflection infrared spectroscopy (FTIR-ATR)

Polarized reflectance of infrared spectroscopy can reveal anisotropy on the molecular level within a sample. This pronounced infrared dichroism (which is the difference in absorption between parallel and perpendicularly polarized light) indicates alignment of molecules, while the absence of diochroism shows that a sample has randomly oriented molecules. Before the sampling process, the PAN fibers were dried at 50 °C for a day in order to remove moisture. IR spectrums of PAN fibers for every sample were recorded using Fourier transform spectrometer (Nicolet Magna-IR 560). The IR spectra were recorded for each sample, one with the electric vector polarized parallel to the stretching direction and another with the electric vector polarized to the stretching direction. The background scans with two different positions of the polarizer were also taken. $A_{\parallel}$ and $A_{\perp}$ are absorbance parallel and perpendicular to the stretch direction. Dichroic ratio (D) is given by the following Eq.,

$$D = A_{\parallel} / A_{\perp}$$

2.3.3. Tensile testing for a tow of fibers

Fiber mechanical properties should be obtained according to ASTM D 3379-75 guidelines. However, the tensile testing machine was not sensitive and failed to give the standard graph of strain versus stress. In addition, the computer program for examining the mechanical properties of polymeric material does not cover the tensile testing of single fiber. Therefore, some modifications had been made in order to obtain the Young's modulus of the PAN fibers. The PAN fibers tow consisting of approximately 200 fibers was wrapped the ends with masking tape, leaving approximately 25 mm gauge length. The load of the tensile testing machine was set to 1 kN and all the samples were then tested using a 100 mm/min crosshead speed. A higher crosshead speed was chosen in order to get clear 'load versus extension gauge length correction' graphs instead of using the recommended crosshead speed at 5 mm/min. The strain and stress were calculated manually using *Excel* spreadsheet and the graph strain versus stress were plotted.

3. Results and discussion

3.1. Modification on conventional spinning process

One of the crucial modifications that introduced during the spinning was to reduce the residence time of PAN fibers in the coagulation bath. This step was necessary since the rate of solvent diffusion from the as-spun fibers to the surrounding medium was absolutely different between the solvent-free coagulation bath and solvent-containing bath. In the solvent-free coagulation bath, the absence of solvent caused the rate of solvent diffusion to rise faster than that of the solvent-containing bath. Delay in the residence time caused a great lost of solvent from the as-spun fiber and consequently produced the PAN fibers with a rigid skin. As a result, the PAN fibers were not able to stand a high jet stretch and led to fiber breakage.

The reduction in residence time is an advantage to the production of PAN fibers. The coagulation bath used to solidify the polymer solution was relatively small compared to that of the conventional spinning system and thus required less amount of coolant for cooling purpose. This will lead to the reduction in the PAN fibers production cost especially in terms of electricity consumption. In addition, the production of PAN fibers could be enhanced by the reduction of operation time.

Apart from the reduction in the residences times, the adjustment in PAN fibers diameter was performed during the coagulation process. At this stage, the as-spun fibers were thinning from 200 to 50 – 70 μm by a draw ratio of 4. This step was essential since the PAN fibers which are small in diameter also contain fewer defects per unit volume and hence possess superior mechanical properties in conformity to the Weibull "weakest link" principle [21]. The stretching process during coagulation process caused a reduction in fiber diameter up to 70 % of the spinneret hole diameter.

In order to investigate the range of residence time, the 18 wt.% polymer solution was used to fabricate the PAN fibers in solvent-free coagulation bath with the temperature of 17 °C. In the present work, the effects of residence

time on the spinning process and properties of PAN fibers were investigated in the range of 2 to 5 s.

3.2. Effects of residence time on the morphology of the PAN fibers

As illustrated in Fig. 2 it is clearly observed that the pore is absent in all cross-section samples except some cracks that exist in the matrix of the cross-section due to a fracture effect (SEM preparation). The absence of pores in the polymer matrix of PAN fibers was due to the synergist effect of the high jet stretch and low residence time. When the spinning dope was immersed into the solvent-free coagulation process, the counter-diffusion of solvent and non-solvent occurred due to the absence of solvent in the coagulation bath even if the spinning process was carried out at low coagulation temperatures. However, a short residence time prevented further inward diffusion of non-solvent towards the center of PAN fibers. As the as-spun PAN fibers continued to lose solvent, they became more concentrated and elastic. As the result, the as-spun PAN fibers were stretched until its diameter was reduced to *ca* 50 – 70 μm. In addition, the high jet stretch helped the outward diffusion of solvent and aligned the polymer chains and this would prevent more non-solvent from diffusing into the core of PAN fibers.

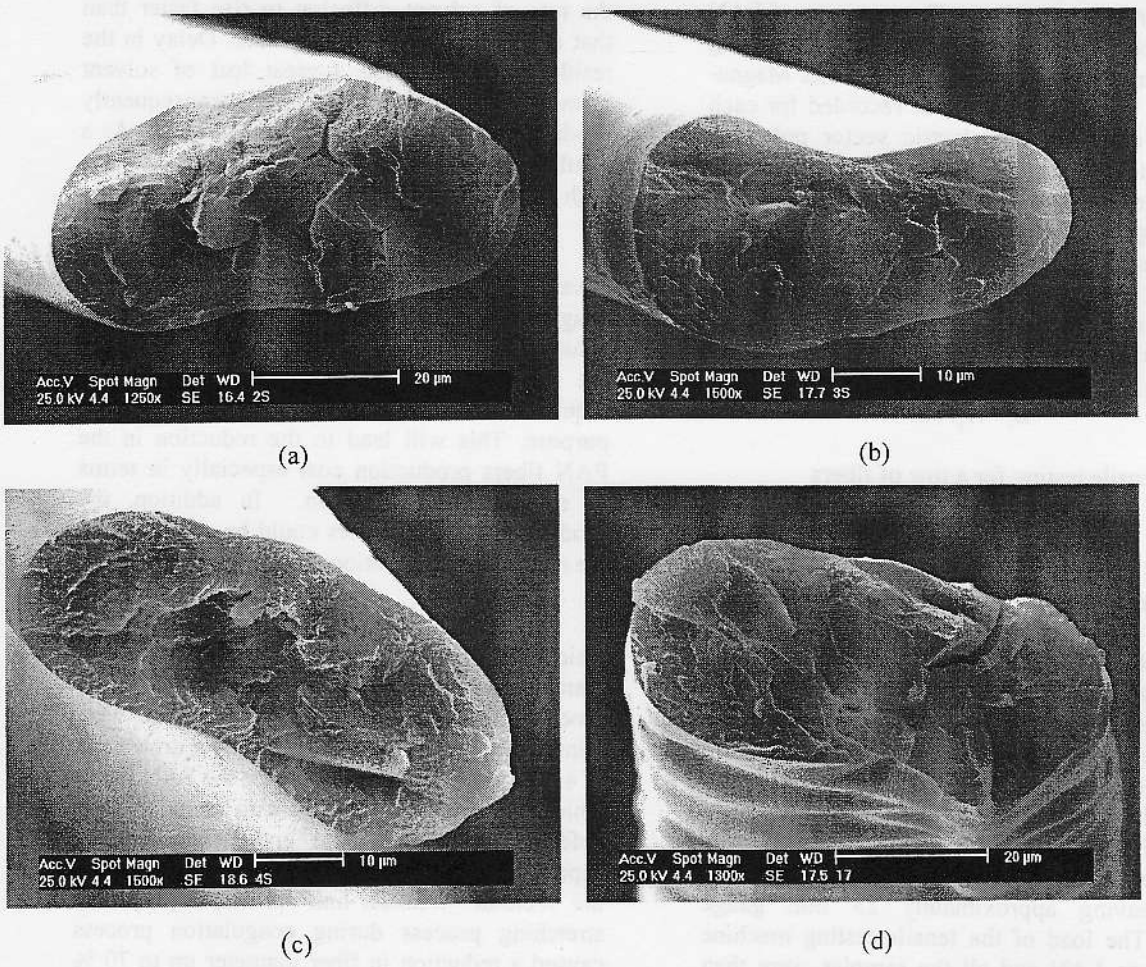

Fig. 2. The cross-section of PAN fibers fabricated at different retention time (a) 2 s, (b) 3 s, (c) 4 s and (d) 5 s

The reduction in residence time during fabrication process did not significantly influence the formation of voids in the matrix of PAN fibers. The formation of void was due to the inward diffusion of non-solvent into the as-spun fibers during coagulation process. Since the residence time was further decreased from 5 to 2 s, the inward diffusion of non-solvent also diminished and there were less amount of non-solvent inside the as-spun fiber. Therefore, it was no possible to observe the void when the residence time was further increased to 2 s.

Table 2 shows the average diameter of PAN fibers for the respective residence time. The PAN fibers fabricated using a residence time of 2 s has an average diameter of 65 μm which is the highest diameter compared to that of other samples. It was probably because the PAN fiber was not fully coagulated. The residence time of 2 s was too low for the solvent from the as-spun fibers to diffuse to the surrounding medium. The residual solvent caused the polymer chains to swell and eventually enlarged the size of PAN fibers. Nevertheless, the average diameter of PAN fibers reduced from 65 to 52 μm when the fabrication process was carried out using a residence time of 3 s. During the fabrication process, the solvent had a sufficient time to diffuse into the coagulation bath and caused a decrease in the PAN fibers size. However, the average diameter of PAN fibers increased from 52 to 63 μm when the residence time was further delayed to 5 s. The increment in the PAN fibers diameter was contributed by the inward diffusion of non-solvent. The higher the residence time, more non-solvent could diffuse towards the PAN fibers.

Table 2
Average residence time of PAN fibers for respective residence time

Residence Time (s)	Average Diameter (μm)
2	65
3	52
4	59
5	63

3.3. Effects of residence time on the Young's modulus of PAN fibers

Fig. 3 illustrates the effect of residence time on the Young's modulus of PAN fibers when the fabrication process was carried out using residences times in the range of 2 to 5 s. The PAN fibers fabricated using the residence time of 2 s have the lowest Young's modulus which is 1.70 GPa compared to other samples fabricated at higher residence time. During the coagulation process, the polymer chains were aligned parallel to the fiber axis and caused the solvent to being pushed away to the surrounding medium of as-spun fibers. However, the residence time of 2 s applied during fiber fabrication process was too low for the solvent removal. Consequently, most of the solvent remained in the as-spun fibers and this caused the polymer chains to swell up. This interrupted the alignment of polymer chains and indirectly reduced the Young's modulus of PAN fibers.

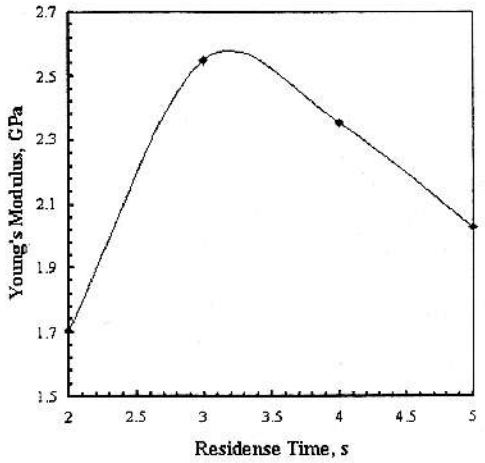

Fig. 3. The change in the Young's modulus of PAN fibers with residence times

However, as residence time was increased from 2 to 3 s, the Young's modulus of PAN fibers increased from 1.7 to 2.55 GPa. During this period, the solvent had enough time to diffuse to the surrounding medium of as-spun fibers which then improved the drawing process and the alignment of polymer chains. The increasing trend of the Young's modulus did not continue once it reached a maximum point at 3 s. As the residence time was further increased to 4 s, the Young's modulus of PAN fibers decreased from 2.55 to 2.35 GPa. The reduction of Young's modulus was probably caused by the presence of micro-pores since the longer the residence time, the higher the amount of non-solvent inside the as-spun fibers. A reduction in the Young's modulus of PAN fibers from 2.35 to 2.02 GPa was observed when the residence time further delayed to 5 s. This reduction was caused

by the existence of micro-pores in a large quantity due to the inward diffusion of non-solvent into the PAN fibers.

3.4. Effects of residence time on the molecular orientation of PAN fibers

Fig. 4 shows the relationship between the residence time and the dichroic ratio of PAN fibers. The dichroic ratio of PAN fibers fabricated at the residence time of 2 s was nearly 1. It described that the molecular orientation of PAN fibers was similar to the orientation of gel fibers [7]. The polymer chains could not be aligned sufficiently since the period for drawing process was too short and consequently caused the PAN fibers to exhibit the lowest Young's modulus. The dichroic ratio of PAN fibers decreased to 0.6, which is the lowest dichroic ratio when the residence time was increased to 3 s. The residence time of 3 s was the optimum immersion and drawing period for fabrication of PAN fibers at a coagulation bath temperature of 17 °C. The solvent from the as-spun fibers had sufficient time to diffuse to the surrounding medium of as-spun fibers during coagulation process which then enhanced the drawing process. The effective drawing process simultaneously increased the mechanical properties and caused the functional groups in the PAN fibers to be oriented along the fiber axis.

As the residence time was further increased to 5 s, the dichroic ratio of PAN fibers also increased. A high residence time caused further outward diffusion of solvent which then concentrated the as-spun fiber. As a result, it disturbed the drawing process and alignment of functional groups. As aforementioned, the Young's modulus of the PAN fibers decreased because of the presence of micro-pores when the residence time was increased from 3 to 5 s. It could also be concluded that the disruption to the alignment of polymer chains as well as in the drawing process reduced the Young's modulus of the PAN fibers.

Fig. 5 shows the relationship between the dichroic ratio and the Young's modulus of PAN fibers fabricated using a polymer solution of 18 wt.% at coagulation bath temperature of 17 °C. The dichroic ratio increased when there was an increment in the Young's modulus of PAN fibers. An improvement in the mechanical properties of the PAN fibers indirectly causes the functional groups to be oriented perpendicularly along the fiber axis. However, this correlation is valid merely if the temperature of the coagulation bath is a constant parameter. A change in the coagulation bath temperature will disturb the correlation since the formation of micro-voids is greatly influenced by the temperature of the coagulation bath.

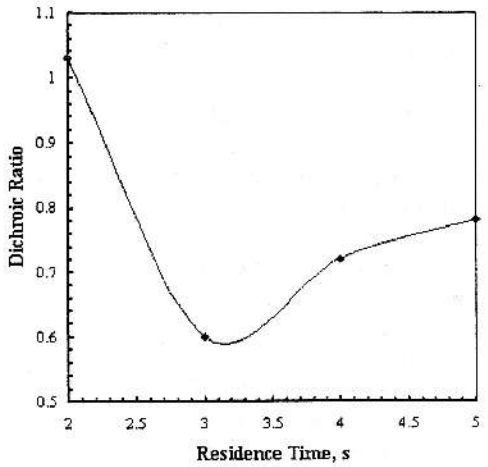

Fig. 4. The change in the dichroic ratio of PAN fibers with residence time

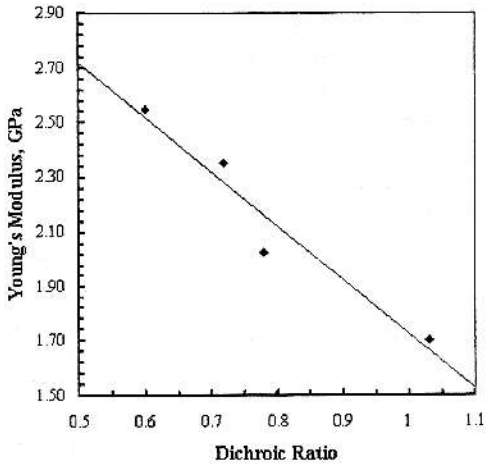

Fig. 5. The relationship between dichroic ratio and Young's modulus at a coagulation bath temperature of 17 °C

4. Conclusion

This study investigated the effects of residence time in the solvent-free coagulation bath on the formation and mechanical properties of PAN fibers. Based on the qualitative analysis,

the shortest residence time for the solvent-free coagulation process is 2 s. An attempt to fabricate the PAN fibers using residence time below 2 s failed since the as-spun fibers were broken as the high jet stretch was introduced during the spinning process. The SEM images revealed the absence of voids for all fiber samples. This is an advantage to the mechanical properties since the voids acted as the weakest link inside the PAN fibers. FTIR-ATR data suggested a high molecular orientation for the PAN fiber fabricated using a residence time of 3 s. In addition, the PAN fibers fabricated using 3 s residence time exhibited the highest Young's modulus.

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